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(54) POLYMERIC ORGANIC ISOCYANATE AND A PROCESS FOR THE PRODUCTION THEREOF

(71) We, **MOBAY CHEMICAL COMPANY**, a corporate body organised under the laws of the State of Delaware, United States of America, of, Penn-Lincoln Parkway West, 5 Pittsburg 4, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to organic isocyanurates and to an improved method for the production of organic isocyanates having an improved stability.

15 Previously it has been proposed to trimerize organic isocyanates, particularly aromatic polyisocyanates in the presence of aliphatic isocyanates, with catalytic amounts of aliphatic, araliphatic or mixed aliphatic-aromatic phosphines. By the use of such a method it has been possible to prepare isocyanurate trimers containing free isocyanate groups, preferably containing both free aromatic and aliphatic NCO groups, which trimers are particularly adaptable for the production of relatively light-stable adhesives, lacquers, elastomers and foams. The proposed process has not, however, been entirely successful since the production of a desirable product depends on terminating the trimerization reaction accurately and quickly at a predetermined point. In the previously known process, the termination of the trimerization reaction has been accomplished by the addition of a neutralizer to the reaction mixture which serves to destroy the catalytic activity of the catalyst. For this purpose, for example, anhydrous hydrogen chloride, benzoyl chloride, acetyl chloride, 40 dimethyl sulfate, methyl-*p*-toluene sulfonate and a mixture of dimethyl sulfate and methyl-*p*-toluene sulfonate have been proposed. The action of these neutralizers is, however, not immediate so that an after-
 45 heating step is generally necessary to com-

plete the deactivation of the catalyst, with the result that the polymerization reaction is not immediately terminated nor is the reaction terminated at the most desirable stage, since the reaction continues for a period of time. Also, when such isocyanurates are prepared using the previously suggested catalyst terminators, the isocyanurate products have tended to deteriorate on storage, and in this results in, for example, undesirable increases in viscosity, and colouration.

It is, therefore, an object of this invention to provide an improved method for the preparation of polymeric isocyanate compositions containing one or more isocyanurate nuclei which reduces or avoids the previously mentioned disadvantages and problems. Another object of this invention is to provide a process for the production of polymeric organic isocyanates of the isocyanurate type by a method in which the polymerization reaction may be substantially immediately terminated upon the addition of a neutralizer to destroy the catalytic activity of the polymerization catalyst. Further objects of this invention are to provide a method for the production of polymeric organic isocyanates without the necessity for an after-heating step after the addition of a catalyst deactivator; to provide an improved method for the production of polymeric organic isocyanates having improved storage stability characteristics; to provide an improved method for the production of polymeric organic isocyanates having improved colour characteristics; and to provide improved polymeric organic isocyanates prepared in accordance with this invention.

The invention accordingly provides a process for the preparation of polymeric isocyanate compositions containing one or more isocyanurate nuclei which comprises the polymerisation of organic isocyanates in the presence of a phosphine catalyst in which pro-

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cess the polymerisation is stopped by the addition of sulphur. In a particularly preferred embodiment of this invention polymeric organic isocyanates are prepared by a process in which aromatic polyisocyanates are trimerized with aliphatic, cycloaliphatic or araliphatic isocyanates, in such proportion that there are at least 0.25 aliphatic-NCO groups present per aromatic-NCO group, in the presence of an organic phosphine catalyst and the polymerisation reaction is terminated by the addition of elemental sulfur. The amount of sulfur employed in the process to terminate the polymerization is a catalyst inhibiting amount, and generally is from an equimolar amount to a 300% molar excess of sulfur based on the weight of catalyst used in the polymerization.

Suitable organic isocyanates which may be used as starting materials for the process of this invention include, for example, aliphatic, cycloaliphatic or aromatic isocyanates or any derivative thereof provided any such derivative contains no substituent which interferes with the reaction, such as those of the formula



in which R is an optionally substituted aliphatic, cycloaliphatic or aromatic hydrocarbon radical and x is an integer of at least 1, generally from 1 to 4, and most preferably from 1 to 3. As examples of suitable aromatic isocyanates there may be mentioned 2,4- and 2,6-toluylene diisocyanate and mixtures thereof, especially a mixture of 80% 2,4- and 20% 2,6-toluylene diisocyanate, 2,4'- and 4,4'- diisocyanato diphenylmethane, as well as m and p-phenylene diisocyanate, 4-tert. butyl-m-phenylene diisocyanate, 1-methoxy-phenylene-2,4-diisocyanate, cumene 2,4-diisocyanate, diphenyl-4,4'-diisocyanate, diphenylether-4,4'-diisocyanate, 2,2-diphenylpropane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate, naphthylene 1,4-diisocyanate, tetrahydronaphthalene-1,5-diisocyanate, naphthalene-2,6-diisocyanate, 3,3'-dimethyldiphenyl-4,4'-diisocyanate, 3,3'-dimethoxydiphenyl-4,4'-diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 2,2'-dimethyldiphenylmethane-4,4'-diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 2,5,2',5'-tetramethyldiphenylmethane-4,4'-diisocyanate, 2,4,4'-triisocyanato diphenylether, 2,4,6-triisocyanato toluene, 4,4',4"-triisocyanato-triphenylmethane, naphthalene-1,3,7 - triisocyanate, diphenylmethane-2,4,6-triisocyanate, 4,4'-dimethyldiphenylmethane-2,2'-5,5'-tetraisocyanate, and tris - (p-isocyanatophenyl) - thiophosphoric acid ester. The aromatic polyisocyanates will generally contain up to 20 carbon atoms.

Any suitable aliphatic, cycloaliphatic or araliphatic polyisocyanate may also be used as a starting material in the process of this

invention, such as for example, methylene diisocyanate, thylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,5-diisocyanato-2,2-dimethylpentane, 1,6-diisocyanato-3-methoxyhexane, decamethylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate and their homologues substituted in the aromatic nucleus, cyclopentylene 1,3-diisocyanate, cyclohexylene 1,3-diisocyanate, 1-methyl - 2,4-diisocyanato - cyclohexane, 1-methyl-2,6-diisocyanato cyclohexane, 4,4'-dicyclomethane diisocyanate, 1,3,5-triisocyanato cyclohexane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane, 2,2',4-trimethyl-6-diisocyanato hexane, 1,4-bis-(3-isocyanatopropoxy)-butane, and 1,4-bis-isocyanatoethyl cyclohexane. Those aliphatic, cycloaliphatic and araliphatic isocyanates containing from 1 to 20 carbon atoms, preferably 2 to 10 carbon atoms, are preferred.

Also it is possible to employ suitable monoisocyanates such as, for example, phenyl isocyanate, benzyl isocyanate, p-tolyl isocyanate, 1-naphthyl isocyanate, n-propyl benzyl isocyanate, o-tolyl isocyanate, p-nitrophenyl isocyanate, p-phenylmethylene phenyl isocyanate, p-methoxy phenylisocyanate, o-chlorophenyl isocyanate, p-chlorophenyl isocyanate, methyl isocyanate, propyl isocyanate, butyl isocyanate, hexyl isocyanate, heptyl isocyanate, decyl isocyanate, octadecyl isocyanate, naphthyl isocyanate, anthrly isocyanate, phenanthrly isocyanate, trichloromethyl isocyanate, 3-chloropropyl isocyanate, 2-ethoxy ethyl isocyanate, and 4-methyl cyclohexyl isocyanate.

The preferred polyisocyanate compositions are prepared according to the process of this invention by the use of 2,4-diisocyanato toluene of mixtures of 2,4-diisocyanato toluene with 2,6-diisocyanato toluene or 1,6-hexamethylene diisocyanate as starting materials or when an aromatic isocyanate is polymerized with an aliphatic, cycloaliphatic or araliphatic isocyanate in such amounts that at least 0.25 aliphatic-NCO groups, preferably more than one -NCO group and most preferably up to 10 aliphatic -NCO groups per aromatic -NCO group are present in the trimerization reaction mixture.

Any suitable phosphine trimerization catalyst may be employed in the process of this invention such as, for example, aliphatic, araliphatic and mixed aliphatic-aromatic phosphines. Suitable examples are trialkyl phosphines such as trimethyl phosphine, triethyl phosphine tri-n-propyl phosphine, triisopropyl phosphine, ethyl dibutyl phosphine, tri-n-butyl phosphine, triisobutyl phosphine, tri-tert.-butyl phosphine, ethyl dimethyl phosphine, methyl diethyl phosphine, propyl dimethyl phosphine, hexyl dimethyl phosphine, diethyl propyl phosphine, ethyl-

di-*tert*.-butyl phosphine, and diethyl butyl phosphine; araliphatic phosphines such as for example tri-benzyl phosphine; and mixed aliphatic-aromatic phosphines such as dimethyl benzyl phosphine, and dimethyl phenyl phosphine. It is also possible to have two alkyl groups linked together to form a ring as in the case of P-butyl-phosphacyclopentane.

The quantity of catalyst used may vary over a wide range. Any catalytic amount, that is, any amount sufficient to catalyze the reaction, may be used. Generally, the amount of catalyst employed will range from 0.001% to 10.0%, preferably from 0.001% to 1.0% and most preferably from 0.01% to 0.1% by weight of the reactants.

The process of this invention can be carried out in the presence or absence of solvents. When solvents are used in carrying out the reaction, the amount of catalyst should be increased. Any suitable inert organic solvent may be employed such as, for example, dioxane, esters such as methyl acetate, ethyl acetate, butyl acetate, methyl glycol acetate, and ethyl glycol acetate, ketones such as acetone, methyl ethyl ketone, diethyl ketone, and cyclohexanone, and benzene hydrocarbons and chlorinated hydrocarbons such as chlorobenzene and chloroform and other suitable aliphatic and aromatic hydrocarbons.

The trimerization reaction can be conducted at any suitable reaction temperature but generally occurs at a temperature of 100° C. or less, generally from -20° C. to 100° C., preferably from 20° C. to 60° C., most preferably at 60° C. or less. Unusually higher temperatures are generally to be avoided to avoid formation of carbodiimides which takes place at these higher temperatures and also to obtain, as far as possible, colourless or only slightly coloured products. The reaction may likewise be conducted at any suitable pressure such as, for example, at atmospheric or superatmospheric pressure but preferably at atmospheric pressure.

Unreacted monomers, catalysts, and catalyst inhibitors can be removed, after the reaction has been stopped, by any suitable separation means, such as, for example, by high vacuum distillation in suitable evaporators, and by extraction with suitable selective solvents in which only monomers but not the trimers are soluble.

The polyisocyanate compositions prepared according to the process of this invention contain one or more isocyanurate nuclei and find particular utility as adhesives and hardening agents for resins. They are further useful in the fabrication of polyester and polyether lacquers and for the production of elastomers and foamed products. The isocyanurates are preferably used in the form

of 50%-70% solid solutions in suitable inert organic solvents such as esters, ketones, hydrocarbons, and chlorinated hydrocarbons such as, for example, ethyl acetate, butyl acetate, ethyl glycol ether acetate, acetone methyl ethyl ketone, cyclohexanone, xylene, 70 dichloromethane, and chlorobenzene.

The invention is illustrated by the following examples in which all parts and percentages are by weight unless otherwise specified.

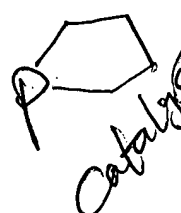
EXAMPLE 1

(1A) In a suitable reactor 1300 parts of an 80/20 mixture of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate are heated at 60° C. with 2600 parts of hexamethylene diisocyanate followed by the addition of 0.78 part of tri-*n*-butyl phosphine. The reaction mixture must be slightly cooled to maintain the temperature at 60° C. After 4.5 hours, when the reaction has reached an NCO value of about 36%, the reaction is stopped by the addition of 1.56 part of a mixture of dimethyl sulphate and methyl-*p*-toluene sulphonate followed by heating for a short period at 100° C. During this period the polymerization reaction continues for a period of time after the mixed neutralizer is added as shown by a drift in the NCO-value. The unreacted monomeric mixture is distilled off by slowly passing the reaction mixture through a thin layer evaporator at a vacuum of 1 mm Hg. at a temperature of the heating medium of from 175° C. to 180° C.

2065 parts of a brittle pale yellow resin having an NCO value of 19.8% are obtained. 1B In a suitable reactor 1300 parts of an 80/20 mixture of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate are heated at 60° C. with 2600 parts of hexamethylene diisocyanate followed by the addition of 0.78 part of tri-*n*-butyl phosphine. The reaction mixture must be cooled slightly to maintain in the temperature at 60° C. After 4.5 hours when the reaction has reached an NCO value of 36%, the reaction is stopped by the addition of 0.2 part of sulfur. No heating is required as the action of the sulfur is immediate. No change of the NCO value is noted after addition of the sulfur. The unreacted monomeric mixture is distilled off by slowly passing the reaction mixture through a thin layer evaporator at a vacuum of 1 mm Hg at a temperature of the heating medium of from 175° C. to 180° C. 2121 parts of a brittle, very pale yellow resin having an NCO value of 20.0% are obtained.

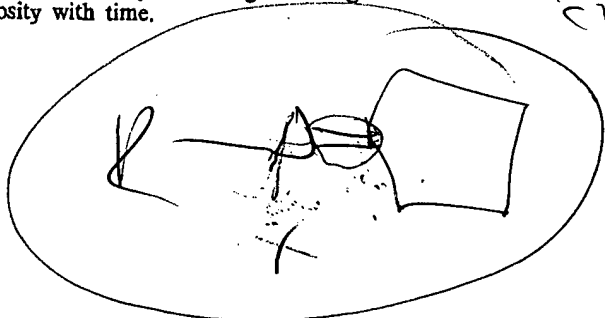
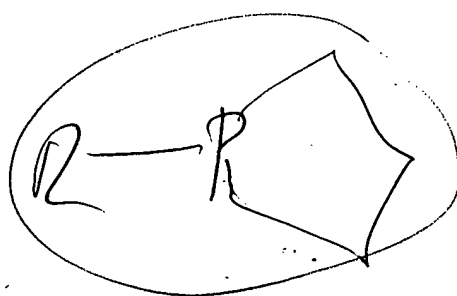
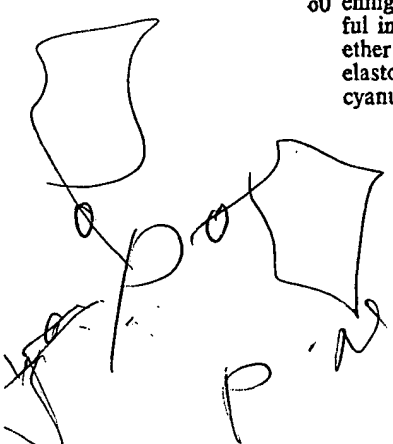
The solid resins from Examples 1A and 1B are dissolved in sufficient ethyl acetate to produce a coating solution containing 60% solids. The stability of the solutions to ageing is evaluated by measuring the change in viscosity with time.

cycloalkyl phosphine



Solvent

tem



aliphatic

Ageing of 60% Solutions

Solution No.	Original Properties			Aged Properties				Colour
	% Solid	% NCO	Viscosity cps at 25° C.	Elapsed Time	Storage Temp.	Viscosity cps at 25° C.	% inc.	Gardner No.
1A	60	11.36	684	21 mo.	ambient	2550	374	5
1B	60	11.75	413	21 mo.	ambient	1170	283	3

15 EXAMPLE 2

When a resin is prepared in the same manner as 1A except that twice the amount of neutralizer, that is, 3.12 parts of methyl *p*-toluene sulphonate and dimethyl sulphate, is employed and a 60% solution in ethyl acetate is prepared therefrom, the solution increases in viscosity from an initial viscosity at 25° C. of 574 cps to a viscosity of 2260 cps at 25° C. after storage at ambient temperature for a period of 21 months. The solution also has a Gardner colour value of 5. The increase in viscosity of the solution is 293% indicating that merely increasing the amount of the previously known neutralizers will not provide satisfactory results. It is thus apparent that neutralization with sulfur gives the lowest rate of increase in viscosity with time in addition to providing a product of improved colour characteristics, that is, the colour of the product is 2 to 3 Gardner Units lighter.

EXAMPLE 3

336 g of hexamethylene diisocyanate are mixed with 1.2 g of tri-*n*-butylphosphine and stirred during 8 hours at from 50 to 60° C. The NCO-content has then dropped from 49.5% to from 35 to 36%. The reaction is stopped by addition of 0.2 g of sulphur. The low viscosity reaction product is distilled twice in a thin layer evaporator (0.3 mm Hg, heating temperature from 160 to 170° C.). There are obtained 161 g of distillate and 170 g of polymer having an NCO-content of 21.1% and a content of free hexamethylene diisocyanate lower than 1%. The IR-spectrum shows absorption peaks at 2.75 - 3.4 - 4.4 - 5.68 - 5.9 - 6.85 - 7.45 - 9.2 - 11.6 - 1275 and 13.04 μ . The characteristic peak of carbodiimides at 4.6 μ cannot be observed. The molecular weight is from 500 to 510.

EXAMPLE 4

3 g of tri-*n*-butylphosphine are added to a stirred solution of 500 g of 2,4-toluylene diisocyanate in 500 g of butylacetate. The temperature rises to from 50 to 60° C. Stirring is continued at this temperature during 30 to 40 hours, after which period of time the NCO-content is from 9.0 to 9.5%. The reaction is stopped by addition of 0.5 g of

sulphur at from 50 to 60° C. Small quantities of non-reacted sulphur, which may be present, are removed by filtration with a pressure filter after cooling the reaction mixture to room temperature.

The products of the process can be used as adhesives, as hardeners for resins and for polyester- and polyether-lacquers, as one-component lacquers and for the production of casting resins, elastomers and foam plastics according to procedures known to those skilled in the art.

WHAT WE CLAIM IS:

1. A process for the preparation of polymeric isocyanate compositions containing one or more isocyanate nuclei which comprises the polymerisation of organic isocyanates in the presence of a phosphine catalyst in which process the polymerisation is stopped by the addition of sulphur.

2. A process as claimed in claim 1 in which organic isocyanates are aromatic or aliphatic isocyanates or are a mixture of aromatic isocyanates with aliphatic isocyanates.

3. A process as claimed in claim 1 or claim 2 in which aromatic polyisocyanates are trimerized with aliphatic, cyclo aliphatic or aliphatic isocyanates in such a proportion that there are at least 0.25 aliphatic -NCO groups present per aromatic NCO group.

4. A process as claimed in claim 3 in which there are up to 10 aliphatic -NCO groups per aromatic-NCO group present.

5. A process as claimed in any one of claims 1 to 4 in which the amount of sulphur employed is a catalyst inhibiting amount.

6. A process as claimed in claim 5 in which the amount of sulphur employed is from an equimolar amount to a 300% molar excess based on the weight of the catalyst.

7. A process as claimed in any one of claims 1 to 6 in which the organic isocyanate has the formula $R(NCO)_x$ in which R is an optionally substituted aliphatic, cycloaliphatic, or aromatic hydrocarbon radical and x is an integer of at least 1.

8. A process as claimed in claim 7 in which x is an integer of from 1 to 3.

9. A process as claimed in any one of claims 1 to 8 in which aliphatic, cycloaliphatic or araliphatic isocyanates are employed which contain from 1 to 20 carbon atoms. 5
10. A process as claimed in claim 9 in which the isocyanates contain from 2 to 10 carbon atoms.
11. A process as claimed in any one of 10 claims 1 to 10 in which the organic isocyanate is 2,4-diisocyanato toluene or a mixture of 2,4-diisocyanato toluene with 2,6-diisocyanato toluene.
12. A process as claimed in any one of 15 claims 1 to 10 in which the organic isocyanate is 1,6-hexamethylene diisocyanate.
13. A process as claimed in any one of claims 1 to 10 in which the organic isocyanate is 2,4-diisocyanato toluene or a mixture of 2,4-diisocyanato toluene with 2,6-diisocyanato toluene in admixture with 1,6-hexamethylene diisocyanate. 20
14. A process as claimed in any one of claims 1 to 13 in which the catalyst is an 25 aliphatic, or an araliphatic or mixed aliphatic-aromatic phosphine.
15. A process as claimed in claim 14 in which the amount of catalyst employed is from 0.01% to 0.1% by weight of the reactants.
16. A process as claimed in any one of claims 1 to 15 in which the process is carried out in the presence of or in the absence of a solvent. 30
17. A process as claimed in any one of claims 1 to 16 in which the reaction temperature is 100°C. or less. 35
18. A process as claimed in claim 17 in which the reaction temperature is 60° C. or less. 40
19. A process for the preparation of polymeric isocyanate compositions containing one or more isocyanurate nuclei substantially as herein described with reference to any one of the Examples. 45
20. Polymeric isocyanate compositions containing one or more isocyanurate nuclei when prepared by a process as claimed in any one of claims 1 to 19.

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